

WHAT IS CLAIMED IS:

1. A polymeric rigid container for foods and beverages which comprises:
  - (a) a polymeric substrate shaped to define a container for a food or a beverage;
  - 5 (b) a first coating layer adhered to at least one surface of the polymeric substrate for retarding the transmission of oxygen and carbon dioxide through the substrate, said first coating layer comprising an organic binder and from 10% up to less than 90% by weight, based on the dry weight of the first coating layer, of an inorganic laminar mineral selected from montmorillonite, laponite, organo-montmorillonite and mixtures thereof, wherein said laminar mineral comprises platelets which are oriented within the first coating layer in a generally parallel three-dimensional and overlapping spaced relationship, and wherein said organic binder is selected from water-soluble or water dispersible organic resins and mixtures thereof; and optionally
  - 10 (c) a second coating layer adhered to said first coating layer which comprises a curable composition comprising a binder component in an organic solvent.
2. A polymeric container according to Claim 1 wherein the water-soluble or water dispersible organic binder of the first coating layer is selected from the
  - 20 group consisting of:
    - (a) homopolyesters; copolyesters; copolyesters derived from a sulpho derivative of a carboxylic acid selected from sulphoterephthalic acid and sulphisophthalic acid;
    - (b) linear or branched acrylic resins having a weight average
      - 25 molecular weight of at least 3000;
    - (c) copolymers of acrylic acid, methacrylic acid and their lower alkyl esters;
    - (d) polyolefins;
    - (e) polysaccharides and cellulosic materials selected from cellulose,
      - 30 hydroxymethyl cellulose, carboxymethyl cellulose, amylose, pluran, starch, and hydroxyethyl cellulose;
    - (f) polyvinyl alcohol;
    - (g) water based aliphatic or aromatic urethanes;
    - (h) ethylene-vinyl alcohol copolymer (EVOH); polyvinylidene
      - 35 dichloride (PVDC); polyacrylonitrile (PAN); and polyethyleimine wherein said polyethyleneimine polymers are of number average molecular weight of from 3000 to 100,000;
    - (i) melamine formaldehyde resin;

- (j) acrylic latices;
- (k) polyvinyl acetate latices;
- (l) polyethylene glycol; and
- (m) blends thereof;

5 and said water soluble or water dispersible organic binder optionally contains (1) a catalyst selected from sulfonic acids, amines, and tin catalysts; and (2) at least one cross-linking agent selected from melamine formaldehyde resin, epoxy resins, isocyanates, aziridenes, carbodiimides, urea formaldehydes, phenolics, silanols, and acids.

10 3. A polymeric container according to Claim 2 in which the water-soluble or water-dispersible organic binder is a blend of (i) melamine formaldehyde resin (including melamine formaldehyde with imino functionality, methylol functionality and partially or highly alkoxy methyl functionality) with (ii) from 5% to 25% by weight, based on the weight of the binder, of an acrylic  
15 latex.

4. A polymeric container according to Claim 2 or Claim 3 in which the binder component of the second coating layer is selected from the group consisting of:

- 20 I. (a) acrylic polymers which contain at least two functional hydroxyl groups and are derived from acrylates, methacrylates, styrene, and hydroxyl functional monomers of such acrylates, said acrylic polymers having a weight average molecular weight of between 3,000 and 50,000;
- (b) polyester resins having at least two functional hydroxyl groups and a weight average molecular weight of from 1000 to 15,000;
- 25 (c) polyester urethanes and acrylo-urethanes having at least two functional hydroxyl groups;
- (d) hydroxyl functional linear or branched cycloaliphatic moiety-containing reactive oligomers or a blend of such oligomers; and
- 30 II. aliphatic or aromatic isocyanates having at least two functional isocyanate groups where the ratio of isocyanate to hydroxyl functionality is from 0.5 to 3.0, based on equivalents.

5. A polymeric container according to Claim 4 in which the polymeric substrate is a polyester selected from polyethylene terephthalate homopolymer or a copolymer of ethylene terephthalate wherein up to about 50 mole percent of the  
35 copolymer is prepared from the monomer units of diethylene glycol; propane-1,3-diol; butane-1,4-diol; polytetramethylene glycol; polyethylene glycol; polypropylene glycol and 1,4-hydroxymethylcyclohexane substituted for the glycol moiety in the preparation of the copolymer; or isophthalic, dibenzoic;

naphthalene 1,4- or 2,6-dicarboxylic; adipic; sebacic; and decane-1,10-dicarboxylic acid substituted for the acid moiety in the preparation of the copolymer.

5 6. A polymeric container according to Claim 5 in which the polyester substrate is a polyethylene terephthalate homopolymer or a copolymer thereof wherein up to 50 mole percent of the copolymer is optionally prepared from isophthalic acid substituted for the acid moiety; the water soluble or water dispersible organic binder of the first coating layer is melamine formaldehyde resin; the inorganic laminar mineral comprises platelets of montmorillonite; and  
10 the second coating layer comprises from 80% to 20% by weight of a binder component which is a blend of a hydroxyl component and an aromatic or aliphatic isocyanate.

7. A polymeric container according to Claim 6 wherein greater than 60% of the laminar mineral platelets have an aspect ratio greater than 150.

15 8. A polymeric container according to Claim 7 which is a biaxially oriented PET bottle.

9. A method for packaging a carbonated liquid in a molded biaxially oriented polyester container which comprises:

- 20 (1) forming the container;
- (2) optionally treating the exterior surface of the container with a means to improve surface adhesion characteristics and thereafter applying to said treated surface a first coating layer having a thickness in the range of 8 microns or less by spraying onto the container surface an aqueous composition comprising a organic binder which is a water soluble or water-dispersible organic binder  
25 selected from the group consisting of:
- (a) homopolyesters; copolyesters; copolyesters derived from a sulpho derivative of a carboxylic acid selected from sulphoterephthalic acid and sulphisophthalic acid;
  - (b) linear or branched acrylic resins having a weight average  
30 molecular weight of at least 3000;
  - (c) copolymers of acrylic acid, methacrylic acid and their lower alkyl esters;
  - (d) polyolefins;
  - (e) polysaccharides and cellulosic materials selected from  
35 cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, amylose, pluran, starch, and hydroxyethyl cellulose;
  - (f) polyvinyl alcohol;
  - (g) water based aliphatic or aromatic urethanes;

(h) ethylene-vinyl alcohol copolymer (EVOH); polyvinylidene dichloride (PVDC); polyacrylonitrile (PAN); and polyethyleimine wherein said polyethyleneimine polymers are of number average molecular weight of from 3000 to 100,000;

- 5                   (i) melamine formaldehyde resin;  
                  (j) acrylic latices;  
                  (k) polyvinyl acetate latices;  
                  (l) polyethylene glycol; and  
                  (m) blends thereof

10   said water soluble or water dispersible organic binder optionally contains (1) a catalyst selected from sulfonic acids, amines, and tin catalysts and (2) at least one cross-linking agent selected from melamine formaldehyde resin, epoxy resins, isocyanates, aziridenes, carbodiimides, urea formaldehydes, phenolics, silanols, and acids, and which contains from 10% to less than 90% by weight, based on the  
15   dry weight of the first coating layer, of an inorganic laminar mineral in the form of platelets and selected from the group consisting of montmorillonite, laponite, organo-montmorillonite and mixtures thereof whereby the platelets orient themselves within the first coating layer in a generally parallel three-dimensional overlapping spaced relationship;

20                   (3) applying to the first coating layer a second coating layer by spraying onto said first coating layer a curable composition comprising a binder component and an organic solvent, wherein the binder component of the second coating layer is selected from the group consisting of:

I. (a) acrylic polymers which contain at least two functional  
25   hydroxyl groups and are derived from acrylates, methacrylates, styrene, and hydroxyl functional monomers of such acrylates, said acrylic polymers having a weight average molecular weight of between 3,000 and 50,000;

                  (b) polyester resins having at least two functional hydroxyl groups and a weight average molecular weight of from 1000 to 15,000;

30                   (c) polyester urethanes and acrylo-urethanes having at least two functional hydroxyl groups;

                  (d) hydroxyl functional linear or branched cycloaliphatic moiety-containing reactive oligomers or a blend of such oligomers; and

II. aliphatic or aromatic isocyanates having at least two  
35   functional isocyanate groups where the ratio of isocyanate to hydroxyl functionality is from 0.5 to 3.0, based on equivalents;

                  (4) curing the second coating layer;

                  (5) introducing a carbonated liquid into the container; and

(6) sealing the container.

10. The method of Claim 9 in which the biaxially oriented polyester container is a polyethylene terephthalate homopolymer or a copolymer thereof wherein up to 50 mole percent of the copolymer is optionally prepared from isophthalic acid substituted for the acid moiety; the water soluble or water dispersible organic binder of the first coating layer is melamine formaldehyde; the inorganic laminar mineral comprises platelets of montmorillonite; and the second coating layer comprises from 80% to 20% by weight of a binder component which is a blend of a hydroxyl component and an aromatic or aliphatic isocyanate.

11. A method for reducing the oxygen and carbon dioxide permeability of a polyester substrate which comprises spraying onto at least one surface of the substrate a generally uniform aqueous coating composition to form a first coating layer which adheres to the substrate, said aqueous composition comprising a water-soluble or water dispersible organic binder in the optional presence of a cross-linking agent and from 10% up to less than 90% by weight, based on the dry weight of the coating layer, of an inorganic laminar mineral selected from montmorillonite, laponite, and mixtures thereof, wherein said laminar mineral comprises platelets, and whereby said platelets move within the organic binder as it is sprayed onto the substrate to form a generally parallel three-dimensional and overlapping spaced relationship in the first coating layer, and wherein said water-soluble or water dispersible organic binder is selected from the group consisting of:

(a) homopolyesters; copolyesters; and copolyesters derived from a sulpho derivative of a carboxylic acid selected from sulphoterephthalic acid and sulphisophthalic acid;

(b) linear or branched acrylic resins having a weight average molecular weight of at least 3000;

(c) copolymers of acrylic acid, methacrylic acid and their lower alkyl esters;

(d) polyolefins;

(e) polysaccharides and cellulosic materials selected from cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, amylose, pluran, starch, and hydroxyethyl cellulose;

(f) polyvinyl alcohol;

(g) water based aliphatic or aromatic urethanes;

(h) ethylene-vinyl alcohol copolymer (EVOH); polyvinylidene dichloride (PVDC); polyacrylonitrile (PAN); and polyethyleimine wherein said

polyethyleneimine polymers are of number average molecular weight of from 3000 to 100,000;

- (i) melamine formaldehyde resin;
- (j) acrylic latices;
- 5 (k) polyvinyl acetate latices;
- (l) polyethylene glycol; and
- (m) blends thereof; and

said water soluble or water dispersible organic binder optionally contains (1) a catalyst selected from sulfonic acids, amines, and tin catalysts and (2) at least one  
10 cross-linking agent selected from melamine formaldehyde resin, epoxy resins, isocyanates, aziridenes, carbodiimides, urea formaldehydes, phenolics, silanols, and acids.

12. The method of Claim 11 which includes the additional steps of:

(1) applying to the first coating layer a second coating layer by  
15 spraying onto said first coating layer a curable composition comprising a binder component and an organic solvent, wherein the binder component of the second coating layer is selected from the group consisting of:

I. (a) acrylic polymers which contain at least two functional hydroxyl groups and are derived from acrylates, methacrylates, styrene, and  
20 hydroxyl functional monomers of such acrylates, said acrylic polymers having a weight average molecular weight of between 3,000 and 50,000;

(b) polyester resins having at least two functional hydroxyl groups and a weight average molecular weight of from 1000 to 15,000;

(c) polyesterurethanes and acrylo-urethanes having at least  
25 two functional hydroxyl groups;

(d) hydroxyl functional linear or branched cycloaliphatic moiety-containing reactive oligomers or a blend of such oligomers; and

II. aliphatic or aromatic isocyanates having at least two functional isocyanate groups where the ratio of isocyanate to hydroxyl  
30 functionality is from 0.5 to 3.0, based on equivalents; and

(2) curing the second coating layer.

13. A water-borne gas barrier coating composition having at least 2% by wt. solids wherein the solids portion of the composition comprises:

(a) from greater than 10% to less than 90% by wt. of a film-forming  
35 water-dispersible or water-soluble organic binder;

(b) from less than 90% to greater than 10% by wt. of an inorganic laminar mineral in the form of platelets selected from montmorillonite, laponite, organo-montmorillonite and mixtures thereof; and, optionally,

(c) from 5% by wt. to 95% by wt., based on the weight of the film-forming water-dispersible or water-soluble organic binder, of a cross-linking agent.

14. The water-borne gas barrier coating composition of Claim 13 wherein the film-forming water-dispersible or water soluble organic binder is selected from the group consisting of:

(a) homopolyesters; copolyesters; copolyesters derived from a sulpho derivative of a carboxylic acid selected from sulphoterephthalic acid and sulphisophthalic acid;

(b) linear or branched acrylic resins having a weight average molecular weight of at least 3000;

(c) copolymers of acrylic acid, methacrylic acid and their lower alkyl esters;

(d) polyolefins;

(e) polysaccharides and cellulosic materials selected from cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, amylose, pluran, starch, and hydroxyethyl cellulose;

(f) polyvinyl alcohol;

(g) water based aliphatic or aromatic urethanes;

(h) ethylene-vinyl alcohol copolymer (EVOH); polyvinylidene dichloride (PVDC); polyacrylonitrile (PAN); and polyethyleimine wherein said polyethyleneimine polymers are of number average molecular weight of from 3000 to 100,000;

(i) melamine formaldehyde resin;

(j) acrylic latices;

(k) polyvinyl acetate latices;

(l) polyethylene glycol; and

(m) blends thereof; and

said water soluble or water dispersible organic binder optionally contains (1) a catalyst selected from sulfonic acids, amines, and tin catalysts and (2) at least one cross-linking agent selected from melamine formaldehyde resin, epoxy resins, isocyanates, aziridenes, carbodiimides, urea formaldehydes, phenolics, silanols, and acids.

15. The water-borne gas barrier coating composition of Claim 14 in which the film-forming water-soluble or water-dispersible organic binder is melamine formaldehyde resin, and the inorganic laminar mineral comprises platelets of montmorillonite having an aspect ratio in the range of 150 or greater.

16. The water-borne gas barrier coating composition of Claim 15 in which the film-forming water-soluble or water-dispersible organic binder is a blend of (i) melamine formaldehyde resin (including melamine formaldehyde with imino functionality, methylol functionality and partially or highly alkoxy methyl functionality) with (ii) from 5% to 25% by weight, based on the weight of the binder, of an acrylic latex.

17. A two-layer coating system for reducing the permeation of oxygen and carbon dioxide through a thermoplastic polymeric substrate which comprises:

I. a first layer having a generally uniform thickness in the range of 8 microns or less and formed by spraying onto the substrate a water-borne composition having at least 2% by wt. solids wherein the solids portion of the composition comprises:

A) from greater than 10% to less than 90% by wt. of a film-forming water-dispersible or water-soluble organic binder selected from the group consisting of:

(a) homopolyesters; copolyesters; copolyesters derived from a sulpho derivative of a carboxylic acid selected from sulphoterephthalic acid and sulphisophthalic acid;

(b) linear or branched acrylic resins having a weight average molecular weight of at least 3000;

(c) copolymers of acrylic acid, methacrylic acid and their lower alkyl esters;

(d) polyolefins;

(e) polysaccharides and cellulosic materials selected from cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, amylose, pluran, starch, and hydroxyethyl cellulose;

(f) polyvinyl alcohol;

(g) water based aliphatic or aromatic urethanes;

(h) ethylene-vinyl alcohol copolymer (EVOH);

polyvinylidene dichloride (PVDC); polyacrylonitrile (PAN); and polyethyleimine wherein said polyethyleneimine polymers are of number average molecular weight of from 3000 to 100,000;

(i) melamine formaldehyde resin;

(j) acrylic latices;

(k) polyvinyl acetate latices;

(l) polyethylene glycol; and

(m) blends thereof; and



B) from less than 90% to greater than 10% by wt. of an inorganic laminar mineral in the form of platelets selected from montmorillonite, laponite, organo-montmorillonite and mixtures thereof; and, optionally,

5 C) from 5% by wt. to 95% by wt., based on the weight of the film-forming water-dispersible or water-soluble organic binder, of a cross-linking agent; and drying and optionally curing the composition whereby the first coating layer adheres to the substrate; and

10 II. a second coating layer having a generally uniform thickness in the range of 12 microns or less and which is formed by spraying onto the first coating layer a curable composition comprising a binder component in an organic solvent, wherein said binder component is selected from the group consisting of:

15 (1) (a) acrylic polymers which contain at least two functional hydroxyl groups and are derived from acrylates, methacrylates, styrene, and hydroxyl functional monomers of such acrylates, said acrylic polymers having a weight average molecular weight of between 3,000 and 50,000;

(b) polyester resins having at least two functional hydroxyl groups and a weight average molecular weight of from 1000 to 15,000;

(c) polyesterurethanes and acrylo-urethanes having at least two functional hydroxyl groups;

20 (d) hydroxyl functional linear or branched cycloaliphatic moiety-containing reactive oligomers or a blend of such oligomers; and

(2) aliphatic or aromatic isocyanates having at least two functional isocyanate groups where the ratio of isocyanate to hydroxyl functionality is from 0.5 to 3.0, based on equivalents; and curing the second  
25 coating layer whereby the second coating layer adheres to the first coating layer.